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Contact Angles of Micro-ellipsoids at Liquid-Liquid Interfaces

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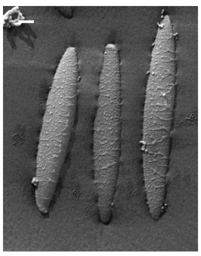
Introduction

The wetting of anisotropic colloidal particles is of great importance in several applications, including Pickering emulsions, filled foams, and membrane transduction by particles. In the present work[1], we **quantify the variation of the contact angle of prolate ellipsoidal colloids at a liquid–liquid interface as a function of surface chemistry and aspect ratio** using Freeze-Fracture Shadow-Casting (FreSCa) cryo-SEM. This method, initially demonstrated for spherical colloids[2], is extended here to the more general case of ellipsoids. Prolate ellipsoidal particles are prepared from polystyrene and poly(methyl methacrylate) spheres using a well-known film stretching technique[3] in which thorough particle cleaning is of the essence. In order to quantify wetting variations with shape a correction term is introduced into the ideal Young–Laplace equation which expresses the relative importance of line effects relative to surface effects. From this term the contribution of an ***effective line tension*** can be extracted. This contribution includes the effects that both surface chemical and topographical heterogeneities have on the contact line and which become increasingly more important for ellipsoids with higher aspect ratios, where the contact line length to contact area ratio increases.

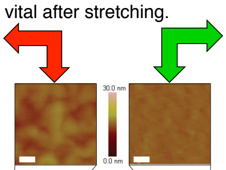
Motivation

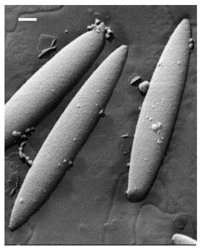
The combined effect of shape and surface chemistry on the three-phase contact angle of anisotropic micrometer and submicrometer colloids has been poorly investigated to date, due to the lack of a suitable experimental technique to resolve individual particles. Techniques such as interferometry[4-6] or gel-trapping combined with SEM[7-9] have a limited in-plane resolution in the former case or need agents which adhere to the particle surface altering its surface chemistry in the latter case.

The importance of proper cleaning: avoiding contact line wrinkling



In order to ensure smooth contact lines with an unarguable contact angle, a proper cleaning method is vital after stretching.



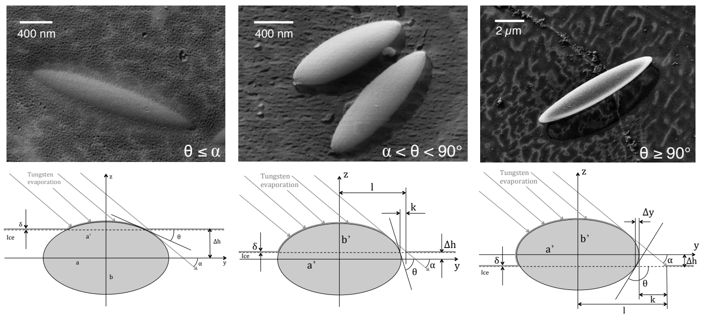


The original cleaning method from Keville *et al.*[3] is unable to remove all PVA residues from the particle surface, causing the particle contact line to wrinkle.

Adding a heating step at 50°C followed by sonication ensures complete removal of all film matrix material as confirmed by SEM and AFM.

'Your identity shall be revealed by your shadow!'

Three possible wetting situations can be distinguished (see images below). In the second and third situation the shadow length combined with the particle dimensions and shadowing angle α are used to calculate the local immersion depth h and from this key parameter the contact angle θ. If a particle finds itself in the first situation, no shadows are available to provide information and thus the average particle dimensions are used instead. An accuracy of 2 – 4° is achieved with this technique.[1]



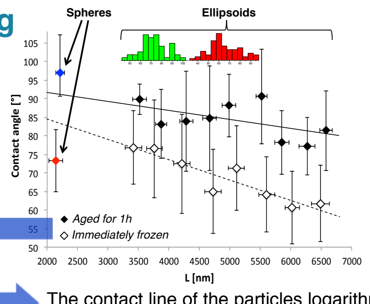
Shape-shifting causes contact angle shifting

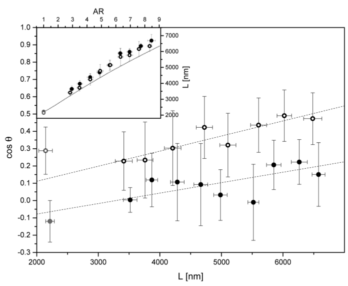
Unaltered particles already show distributions with deviations of 7 – 9°.

Varying the aspect ratio (AR) of PS sulfate latex ellipsoids, a small gradual decreasing trend of θ with AR is revealed. When plotting cos(θ) as a function of contact line length (L) a similar increase with L is observed.[1]

→ introduction of an *effective line tension* τ', collecting contributions from surface energy, surface topography and actual line tension:

$$\underbrace{\cos\theta \approx \cos\theta_0}_{\text{from ideal Young's law}} + \underbrace{kL}_{\text{correction term}} \quad , \quad \underbrace{k \sim \frac{\tau'}{\gamma\pi R^2}}_{\text{by comparison with generalized Young's equation[10]}} \longrightarrow \underbrace{\tau' \sim 10^{-9}\,\mathrm{N}}_{\textit{effective}\text{ line tension}}$$





The contact line of the particles logarithmically relaxes towards equilibrium (aging effect). In addition, Young's equation can only be applied on particles which are fully equilibrated. Therefore, the linearization is only valid for particle contact lines which have aged sufficiently (as those with closed symbols in the graphs above).

Conclusions

FreSCa cryo-SEM is able to visualize the contact line of spherical and ellipsoidal particles at a liquid–liquid interface with nanometer resolution and measure their contact angle with 2 – 4° accuracy on both hydrophilic (PS) and hydrophobic (PMMA) particles.
Surface contaminants induce heterogeneous wetting and corrugations of the contact line, obstructing an accurate contact angle determination.
By comparing the contact angle of ellipsoids a small gradual decrease of θ with increasing aspect ratio is revealed. Introducing a correction term allows writing a linearized version of the generalized Young-Laplace equation, combining contributions from contact line heterogeneities and possible surface energy changes into an *effective* line tension, which becomes more important for particles with higher aspect ratios. Aging effects must be considered when applying this correction.

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